

UNITED STATES PATENT APPLICATION
OF
STEPHANE SABELLE, LAURE RAMOS, AND MADELEINE LEDUC
FOR
BIS-PARA-PHENYLENEDIAMINE DERIVATIVES COMPRISING A PYRROLIDYL
GROUP AND USE OF THESE DERIVATIVES FOR DYEING KERATIN FIBRES

[001] This application claims benefit of U.S. Provisional Application No. 60/431,713, filed December 9, 2002.

[002] The disclosure herein relates to novel bis-para-phenylenediamine derivatives comprising a pyrrolidyl group, as well as to dye compositions comprising the derivatives disclosed herein, and to the process of dyeing keratin fibres using these compositions.

[003] It is known practice to dye keratin fibres, for example human hair, with dye compositions containing oxidation dye precursors, such as ortho- or para-phenylenediamines, ortho- or para-aminophenols, heterocyclic compounds such as diaminopyrazole derivatives, pyrazolo[1,5-a]pyrimidine derivatives, pyrimidine derivatives, pyridine derivatives, 5,6-dihydroxyindole derivatives and 5,6-dihydroxyindoline derivatives, which are generally known as oxidation bases. Oxidation dye precursors, or oxidation bases, are colourless or weakly coloured compounds that, when combined with oxidizing products, may give rise to coloured compounds and dyes by a process of oxidative condensation.

[004] It is also known that the shades obtained with these oxidation bases may be varied by combining them with couplers or coloration modifiers, the latter being chosen, for example, from aromatic meta-diamines, meta-aminophenols, meta-hydroxyphenols and certain heterocyclic compounds, for instance pyrazolo[1,5-b]-1,2,4-triazole derivatives, pyrazolo[3,2-c]-1,2,4-triazole derivatives, pyrazolo[1,5-a]pyrimidine derivatives, pyridine derivatives, pyrazol-5-one derivatives, indoline derivatives and indole derivatives.

[005] The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained.

[006] The “permanent” coloration obtained using oxidation dyes may satisfy a certain number of requirements. It should have no toxicological drawback, be capable of producing shades in the desired intensity, and it show good resistance to external agents (such as, light, bad weather, washing, permanent-waving, perspiration and rubbing).

[007] The dyes can also be able to cover grey hair and they can be as unselective as possible, i.e. they can produce the smallest possible differences in coloration along the same keratin fibre, which may in fact be differently sensitized (i.e. damaged) between its end and its root. They can also show good chemical stability in formulations and have a good toxicological profile.

[008] In the field of hair dyeing, para-phenylenediamine and para-tolylenediamine are oxidation bases that are widely used. They make it possible with oxidation couplers to obtain varied shades.

[009] However, there is a need for new oxidation bases that have a better toxicological profile than para-phenylenediamine and para-tolylenediamine, while at the same time giving the hair excellent properties in terms of colour intensity, variety of shade, colour uniformity and resistance to external agents.

[010] It is known practice to use para-phenylenediamine derivatives substituted with a pyrrolidine group as oxidation bases for colouring keratin fibres. For example, patent U.S. Pat. No. 5,851,237 describes the use of 1-(4-aminophenyl)pyrrolidine derivatives optionally substituted on the benzene nucleus, as replacements for para-phenylenediamine. U.S. Pat. No. 5,993,491 proposes the use of N-(4-aminophenyl)-2-hydroxymethylpyrrolidine derivatives optionally substituted on the benzene nucleus and on the pyrrolidine heterocycle, in position 4, with a hydroxyl radical, as replacement for para-

phenylenediamine. U.S. Pat. No. 5,876,464 describes para-phenylenediamine derivatives substituted with a pyrrolidine group bearing a carbamoyl radical in position 2.

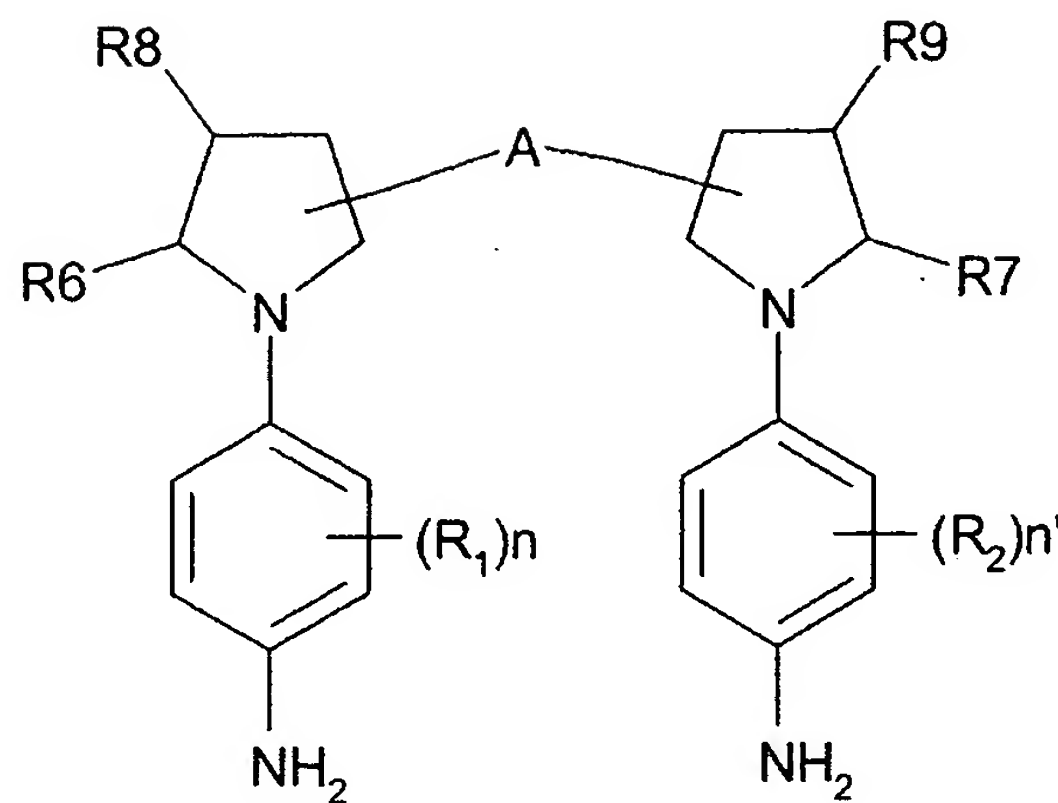
[011] Patent application JP 11-158 048 proposes compositions containing at least one compound chosen from 4-aminoaniline derivatives optionally substituted on the benzene nucleus, one of the nitrogen atoms of which is included in a 5- to 7-membered carbon-based ring. Document WO 02/45675 describes para-phenylenediamine derivatives substituted with a pyrrolidine radical bearing a particular quaternary ammonium group.

[012] It is clearly established that these previously proposed compounds cannot give the hair a coloration equivalent in quality to that obtained with para-phenylenediamine or with para-tolylenediamine, due to the lack of colour intensity and colour uniformity.

[013] There is thus a real need to discover novel oxidation bases that have both a good toxicological profile and properties such that the compositions comprising them can give the hair excellent properties in terms of colour intensity, variety of shades, colour uniformity and resistance to the various external attacks to which the hair may be subjected.

[014] Disclosed herein are novel dye compositions that do not have some of the drawbacks of the oxidation bases of the prior art, and are suitable for dyeing keratin fibres that are capable of producing intense colorations in varied shades, which can be sparingly selective and particularly resistant, and which have a good toxicological profile.

[015] Thus, one aspect of the disclosure herein is bis-para-phenylenediamine derivatives substituted with a pyrrolidyl group, wherein the derivatives are chosen from those of formula (I), and the addition salts thereof:



(I)

wherein:

- n and n', which may be identical or different, are integers ranging from 0 to 4, wherein if either n or n' is greater than or equal to 2, then R₁ and R₂ may be identical or different;
- R₁ and R₂, which may be identical or different, are each chosen from halogen atoms, and C₁-C₆ hydrocarbon-based chains which may be aliphatic, alicyclic, saturated or unsaturated, wherein at least one of the carbon atoms of the chain may optionally be replaced with at least one entity chosen from oxygen, nitrogen, silicon, and sulphur atoms, SO groups, and SO₂ groups, with the proviso that R₁ and R₂ do not comprise a peroxide bond or diazo, nitro, or nitroso radicals, and wherein the chain may be substituted with at least one entity chosen from halogen atoms and hydroxyl, C₁-C₆ alkoxy, amino, mono-, di(C₁-C₆)alkylamino and tri(C₁-C₆)alkylammonium radicals, and N-(C₁-C₆)alkylimidazolinium radicals;
- A is chosen from a covalent bond, and alkylene chains comprising from 1 to 14 carbon atoms, wherein the chains may be linear, branched, saturated or unsaturated, and wherein at least one of the carbon atoms of the chain may optionally be replaced with an entity chosen from: onium radical Z, oxygen, sulphur, silicon and nitrogen atoms,

and CO, SO, and SO₂ groups, wherein the alkylene chains may optionally be substituted with at least one entity chosen from: halogen atoms, hydroxyl, C₁-C₆ alkoxy, amino, (C₁-C₆)alkylamino, and di(C₁-C₆)alkylamino radicals;

- R₆ and R₇, which may be identical or different, are chosen from: hydrogen atoms; carboxyl radicals; (C₁-C₄)alkylcarboxyl radicals; carbamoyl radicals; (C₁-C₄)(alkyl)carbamoyl radicals; (dialkyl)carbamoyl radicals; tri(C₁-C₆)alkylsilane radicals; tri((C₁-C₆)alkyl)ammonium radicals; N-(C₁-C₆)alkylimidazolinium radicals; C₁-C₁₅ alkyl radicals; C₁-C₁₅ alkyl radicals which may optionally be unsaturated, and/or substituted with at least one entity chosen from hydroxyl, (C₁-C₆)alkyloxy, amino, mono- and di(C₁-C₆)alkylamino, thiol, and (C₁-C₆)alkylsulphonic radicals, and halogen atoms; C₁-C₁₅ alkyl radicals which may optionally be unsaturated and/or substituted with at least one radical chosen from carboxylic, (C₁-C₆)alkylcarbonyl, (C₁-C₆)alkoxycarbonyl, carbamoyl, mono- or di(C₁-C₆)alkylcarbamoyl, tri(C₁-C₆)alkylsilane, tri((C₁-C₆)alkyl)ammonium and N-(C₁-C₆)alkylimidazolinium radicals;
- R₈ and R₉, which may be identical or different, are chosen from: hydrogen atoms; hydroxyl radicals; (C₁-C₄)alkyloxy radicals; amino radicals; mono- and di(C₁-C₄)alkylamino radicals; thiol radicals; carboxyl radicals; (C₁-C₄)alkylcarboxyl radicals; carbamoyl radicals; (C₁-C₄)(alkyl and/or dialkyl)carbamoyl radicals; tri(C₁-C₆)alkylsilane radicals; tri((C₁-C₆)alkyl)ammonium radicals; N-(C₁-C₆)alkylimidazolinium radicals; C₁-C₁₅ alkyl radicals; C₁-C₁₅ alkyl radicals which may optionally be unsaturated and/or substituted with at least one entity chosen from: hydroxyl, (C₁-C₆)alkyloxy, amino, mono- and/or di(C₁-C₆)alkylamino, thiol, and (C₁-C₆)alkylsulphonic radicals, and halogen atoms; C₁-C₁₅ alkyl radicals which may optionally be unsaturated, and/or substituted with at least one radical chosen from: carboxylic, (C₁-C₆)alkylcarbonyl, (C₁-

C₆)alkoxycarbonyl, carbamoyl, mono- and/or di(C₁-C₆)alkylcarbamoyl, tri(C₁-C₆)alkylsilane, tri((C₁-C₆)alkyl)ammonium, and N-(C₁-C₆)alkylimidazolinium radicals.

[016] Also disclosed herein is a dye composition comprising at least one bis-para-phenylenediamine derivative of formula (I) as an oxidation base. Still further disclosed herein is the use of this composition for dyeing keratin fibres, as well as a process for dyeing keratin fibres, for example, human keratin fibres such as the hair, using the composition of the present invention.

[017] The composition of the present disclosure makes it possible, for instance, to obtain chromatic, powerful, sparingly selective and colourfast coloration of keratin fibres.

[018] In the context of the present disclosure, an aliphatic hydrocarbon-based chain can be a linear or branched chain that may contain unsaturations of alkene or alkyne type. An alicyclic hydrocarbon-based chain is a saturated or unsaturated branched chain containing no aromatic cyclic structure.

[019] When the chain is interrupted with an oxygen, sulphur, nitrogen or silicon atom T or SO₂, a unit CH₂-T-CH₂, -T-, etc. is obtained, for example.

[020] By way of example, R₁ and R₂, which may be identical or different, may be chosen from chlorine and bromine atoms, and methyl, ethyl, isopropyl, vinyl, allyl, methoxymethyl, hydroxyethyl, 1-carboxymethyl, 1-aminomethyl, 2-carboxyethyl, 2-hydroxyethyl, 3-hydroxypropyl, 1,2-dihydroxyethyl, 1-hydroxy-2-aminoethyl, 1-amino-2-hydroxyethyl, 1,2-diaminoethyl, methoxy, ethoxy, allyloxy and 2-hydroxyethyloxy radicals.

[021] According to one aspect of the disclosure, R₁ and R₂, which may be identical or different, are chosen from chlorine, bromine, C₁-C₄ alkyl radicals, C₁-C₄ hydroxyalkyl radicals, C₁-C₄ aminoalkyl radicals, C₁-C₄ alkoxy radicals, C₁-C₄ hydroxyalkoxy radicals,

tri(C₁-C₄)alkylammonium(C₁-C₄)alkyl radicals and N-(C₁-C₄)alkylimidazolinium(C₁-C₄)alkyl radicals. For example, R₁ and R₂ can be chosen from methyl, isopropyl, tert-butyl, hydroxymethyl, 2-hydroxyethyl, 1,2-dihydroxyethyl, methoxy, isopropoxy, 2-hydroxyethoxy, trimethylammoniummethyl and N-methylimidazolinium radicals.

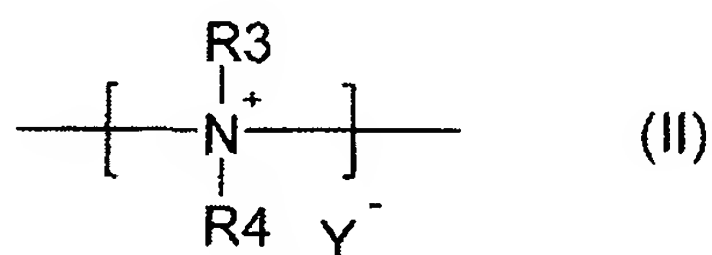
[022] In formula (I), n and n' are independently 0 or 1.

[023] According to another aspect of the disclosure, A does not comprise a peroxide bond, or a diazo, nitro or nitroso radical.

[024] A can be, for example, a covalent bond or an alkylene chain containing from 1 to 8 carbon atoms. According to another aspect of the disclosure, A is an alkylene chain comprising from 1 to 8 carbon atoms, wherein one or more of the carbon atoms of the chain can optionally be replaced with a nitrogen atom and/or an oxygen atom. A can represent an alkylene chain, one or more of the carbon atoms of which chain may be replaced with a nitrogen atom and/or an oxygen atom, and comprising one or more onium radicals Z.

[025] The term "onium" means a nitrogen-based quaternary radical.

[026] According to one aspect of the disclosure, the onium radical Z corresponds to formula (II):

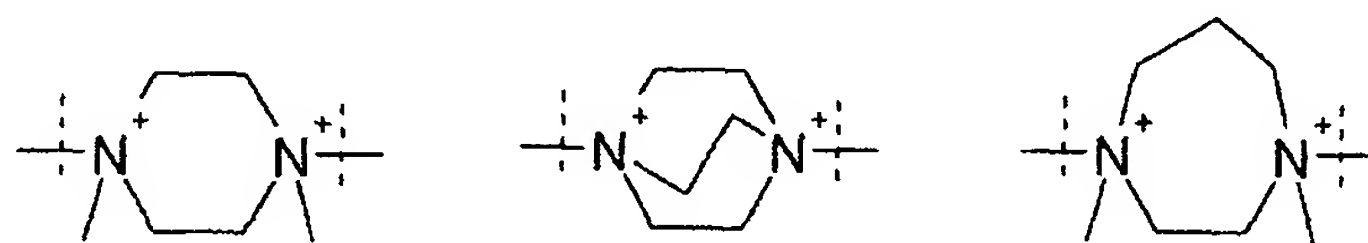


wherein:

- Y⁻ is a counterion;

- R_3 and R_4 , which may be identical or different, are chosen from C_1 - C_{15} alkyl radicals; C_1 - C_6 monohydroxyalkyl radicals; C_2 - C_6 polyhydroxyalkyl radicals; $(C_1$ - $C_6)$ alkoxy(C_1 - C_6)alkyl radicals; aryl radicals; benzyl radicals; amido(C_1 - C_6)alkyl radicals; tri(C_1 - C_6)alkylsilane(C_1 - C_6)alkyl radicals; C_1 - C_6 aminoalkyl radicals; C_1 - C_6 aminoalkyl radicals, wherein the amines are mono- and/or disubstituted with at least one entity chosen from C_1 - C_4 alkyl, $(C_1$ - $C_6)$ alkylcarbonyl, amido and $(C_1$ - $C_6)$ alkylsulphonyl radicals;
- R_3 and R_4 , together with the nitrogen atom to which they are attached, form a 5-, 6- or 7-membered heterocycle; and
- when at least two onium radicals of formula (II) are present in the chain A, at least one of the radicals R_3 and R_4 of one of the onium radicals may form a cyclic diammonium structure with at least one of the radicals R_3 and R_4 of the at least one other onium radical.

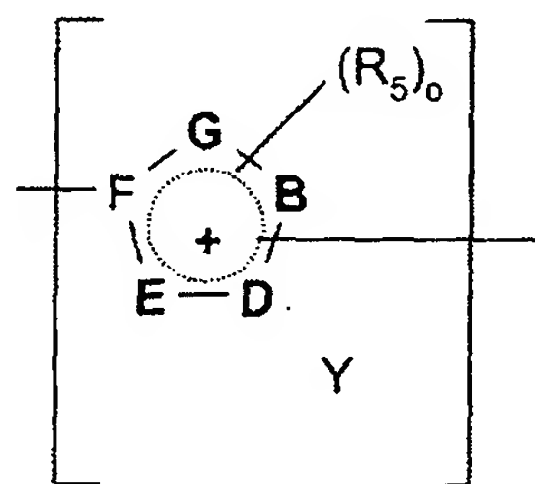
[027] In the latter case, the structures that are obtained by linking together two groups R_3 or R_4 of two onium radicals present in chain A are, for example:



[028] R_3 and R_4 , which may be identical or different, may be chosen, for example, from C_1 - C_4 alkyl radicals and C_1 - C_4 hydroxyalkyl radicals. They may also together form a cationic pyrrolidinium, piperidinium, piperazinium or morpholinium ring, the cationic ring possibly being substituted with an entity chosen from halogen atoms and hydroxyl, C_1 - C_6 alkyl, C_1 - C_6 monohydroxyalkyl, C_2 - C_6 polyhydroxyalkyl, C_1 - C_6 alkoxy, tri(C_1 - C_6)alkylsilane(C_1 - C_6)alkyl, amido, carboxyl, $(C_1$ - $C_6)$ alkyl, thio, C_1 - C_6 thioalkyl, $(C_1$ -

C₆)alkylthio, amino, amino mono- or disubstituted with a (C₁-C₆)alkyl radical, (C₁-C₆)alkylcarbonyl, amido and (C₁-C₆)alkylsulphonyl radicals. By way of example, R₃ and R₄ together may form a cationic pyrrolidinium, piperidinium or morpholinium ring.

[029] The onium radical Z may also be a radical of formula (III):



(III)

wherein:

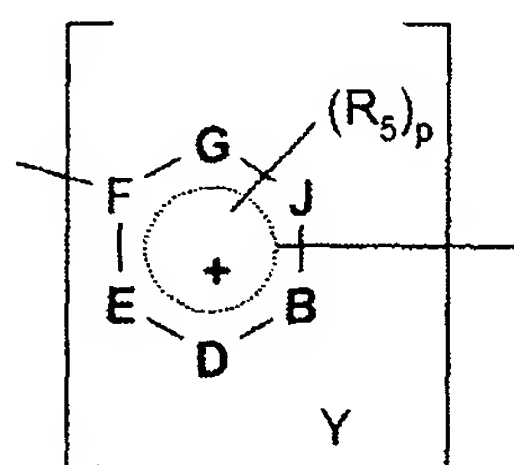
- the ring members B, D, E, F and G, which may be identical or different, are chosen from carbon, oxygen, sulphur and nitrogen atoms, such that B, D, E, F, and G are selected so as to form an aromatic ring cationized on the nitrogen, wherein the ring is chosen from pyrrolium, pyrazolium, imidazolium, triazolium, oxazolium, isoxazolium, thiazolium and isothiazolium rings;
- o is an integer ranging from 0 to 4 ;
- R₅, which may be identical or different, is chosen from C₁-C₆ alkyl radicals, C₁-C₆ monohydroxyalkyl radicals, C₂-C₆ polyhydroxyalkyl radicals, tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl radicals, (C₁-C₆)alkoxy(C₁-C₆)alkyl radicals, carbamyl(C₁-C₆)alkyl radicals, (C₁-C₆)alkylcarboxy(C₁-C₆)alkyl radicals and benzyl radicals; and further wherein the at least one radical R₅ is attached to a carbon, R₅ may also be a radical chosen from

hydroxyl, (C₁-C₄)alkyloxy, amino, (C₁-C₄)alkylamino and di(C₁-C₄)alkylamino radicals, and

- Y⁻ is a counterion.

[030] In one aspect of the disclosure, for example, Z is chosen from an imidazolium ring and a thiazolium ring.

[031] The onium radical Z may also be a radical of formula (IV):



(IV)

wherein:

- the ring members B, D, E, F, G and J, which may be identical or different, are chosen from carbon and nitrogen atoms, such that B, D, E, F, G, and J are selected so as to form an aromatic ring cationized on the nitrogen, wherein the ring is chosen from pyridinium, pyrimidinium, pyrazinium, triazinium and pyridazinium rings;
- p is an integer from 0 to 4 ;
- R₅, which may be identical or different, is chosen from C₁-C₆ alkyl radicals, C₁-C₆ monohydroxyalkyl radicals, C₂-C₆ polyhydroxyalkyl radicals, tri(C₁-C₆)alkylsilane(C₁-C₆)alkyl radicals, (C₁-C₆)alkoxy(C₁-C₆)alkyl radicals, carbamyl(C₁-C₆)alkyl radicals, (C₁-C₆)alkylcarboxy(C₁-C₆)alkyl radicals and benzyl radicals; and where the at least one

radical R₅ is attached to a ring member chosen from carbon, R₅ may optionally be a radical chosen from hydroxyl, (C₁-C₄)alkyloxy, (C₁-C₄)alkylamino and di(C₁-C₄)alkylamino radicals, and

- Y⁻ represents a counterion.

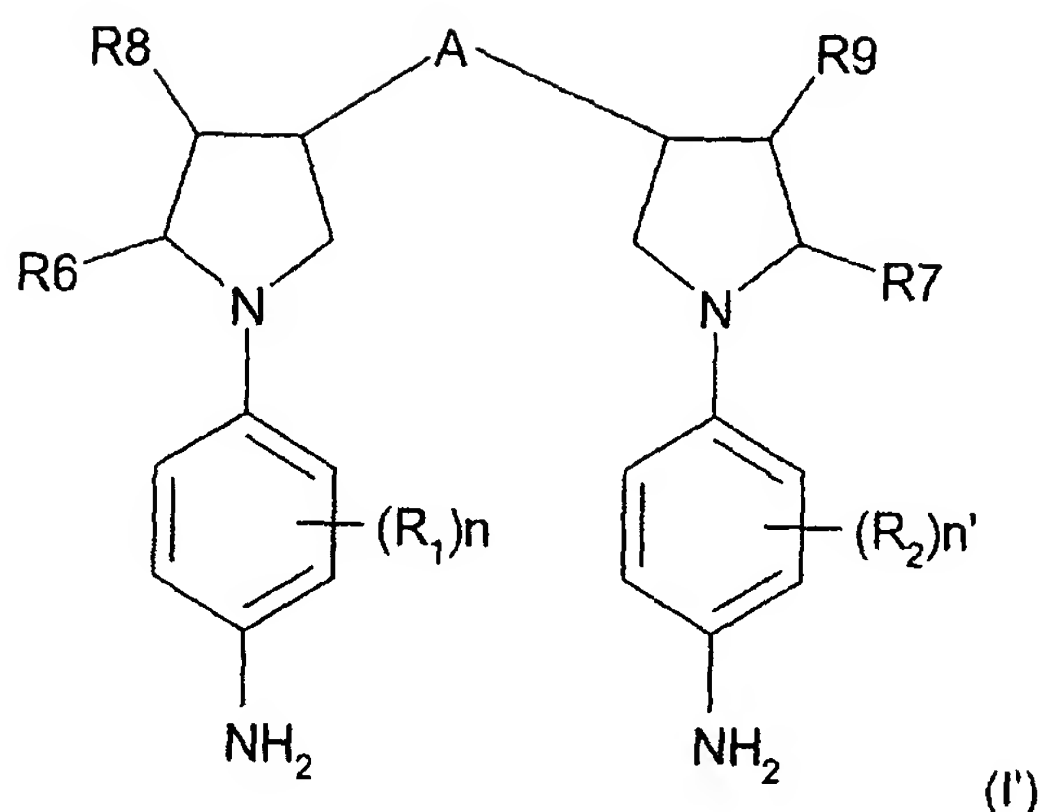
[032] In another aspect of this disclosure, the onium radical Z of formula (IV) is, for instance, a cationized pyridinium ring.

[033] In the context of the present disclosure, R₅ is, for example, a C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl radical.

[034] By way of non-limiting illustration, R₆ and R₇ may be chosen from hydrogen, a C₁-C₄ hydroxyalkyl radical, for example hydroxymethyl, a C₁-C₄ alkyl radical, for example methyl, a carboxyl radical, a carbamoyl radical, a mono- or di(C₁-C₄)alkylcarbamoyl radical, for example N,N-dimethylcarbamoyl, a tri(C₁-C₄)alkylammonium(C₁-C₄)alkyl radical, for example trimethylammoniummethyl, or an N-(C₁-C₄)alkylimidazolium(C₁-C₄)alkyl radical.

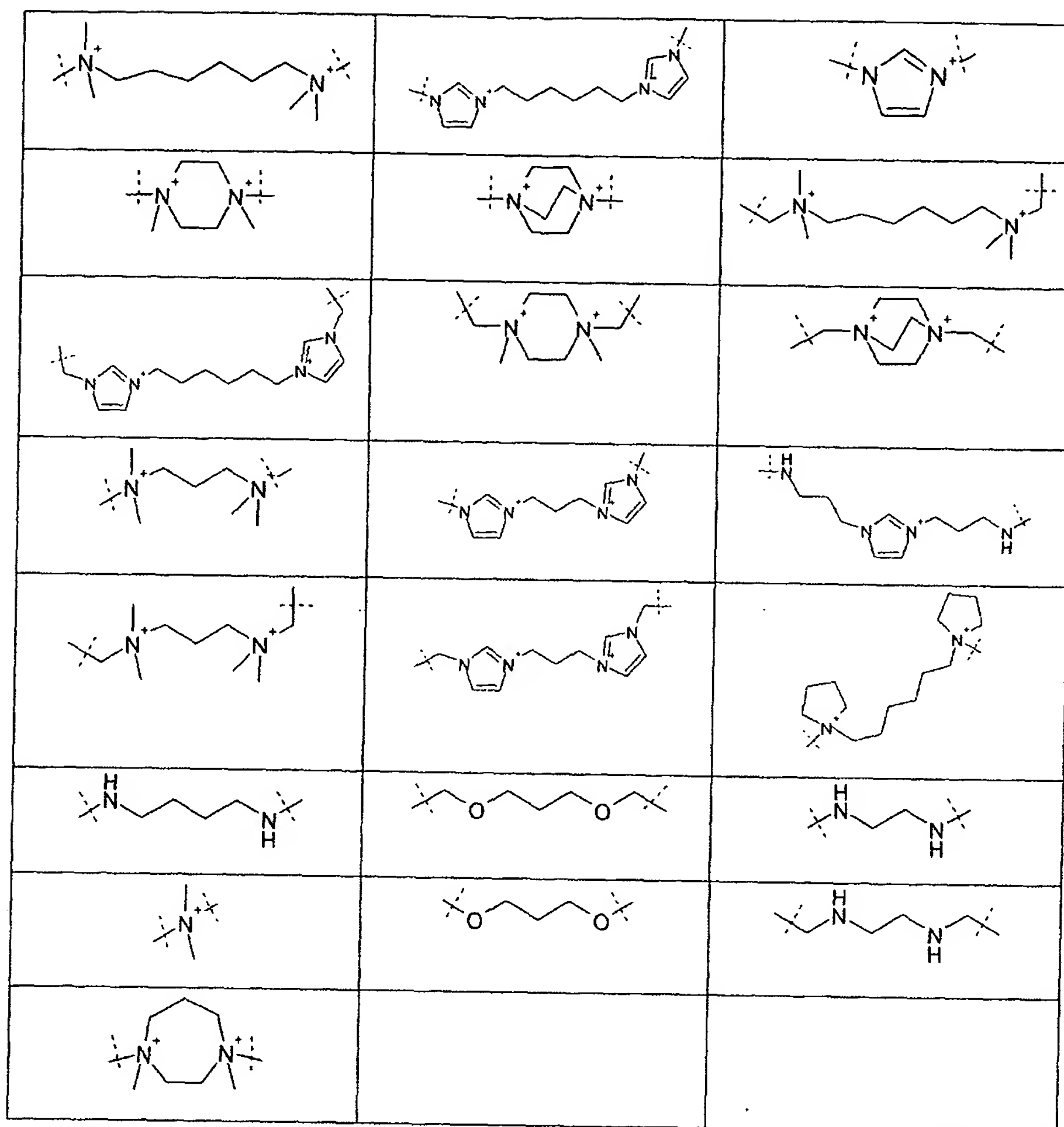
[035] For further example, R₈ and R₉ may be chosen from hydrogen, a hydroxyl radical, an amino radical, a mono- or di(C₁-C₄)alkylamino radical, for example dimethylamino or bis(2-hydroxyethyl)amino, a C₁-C₄ alkyl radical, for example methyl, a tri(C₁-C₄)alkylammonium radical, for example trimethylammonium, or an N-(C₁-C₄)alkylimidazolium radical, for example N-methylimidazolium.

[036] According to another aspect of the disclosure, the derivatives of the invention are chosen from those of formula (I') below



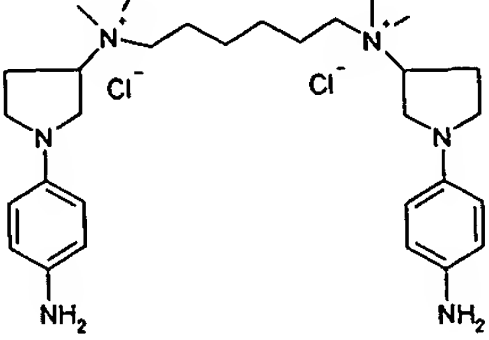
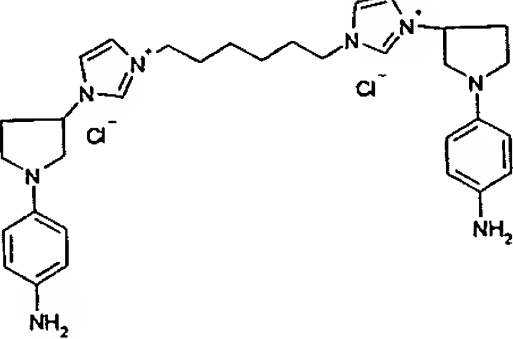
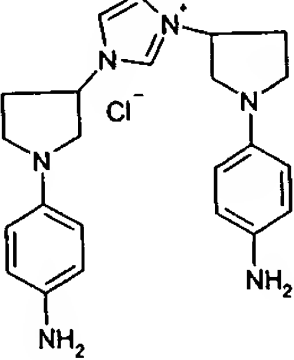
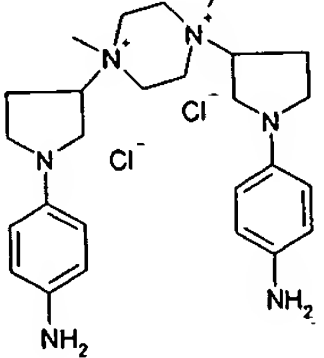
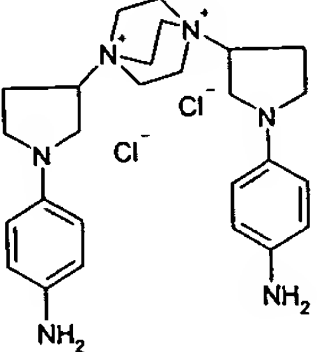
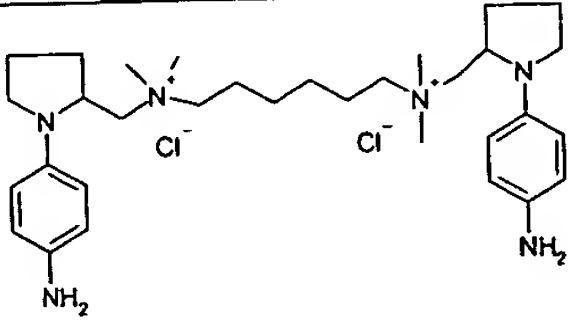
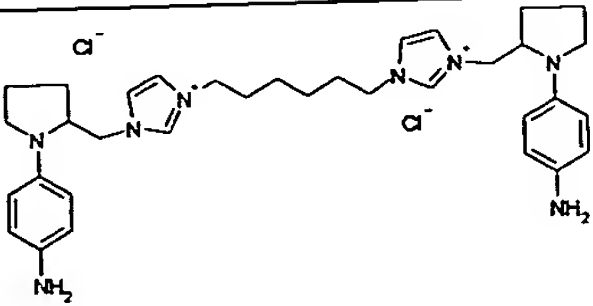
wherein R_1 , R_2 , n , n' , R_6 , R_7 , R_8 , R_9 and A are as defined above.

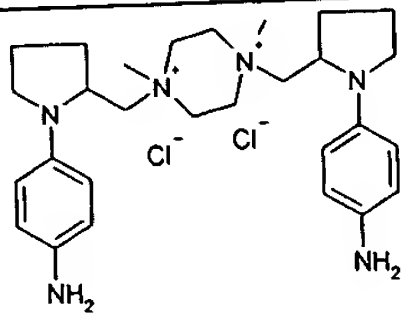
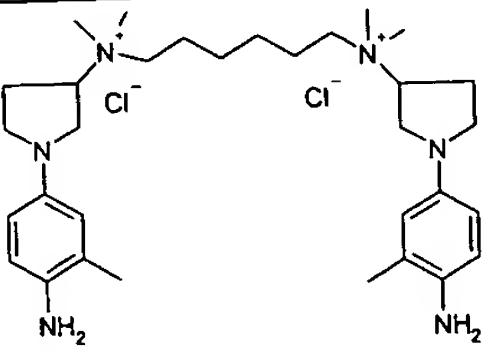
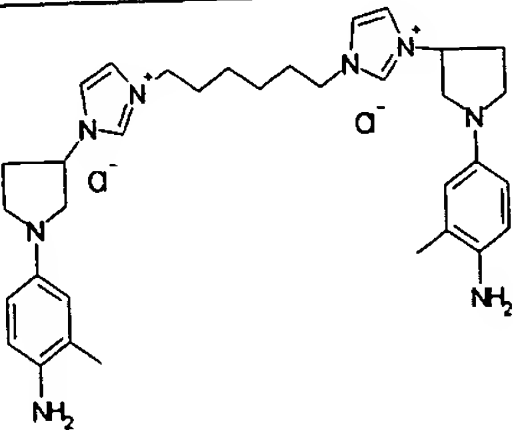
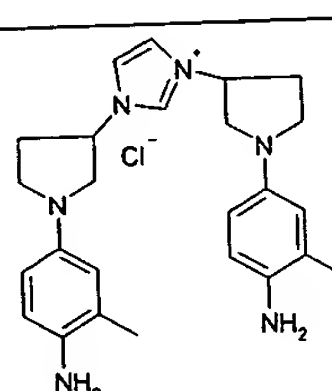
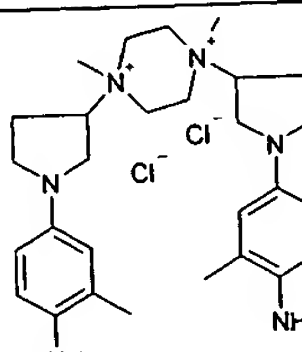
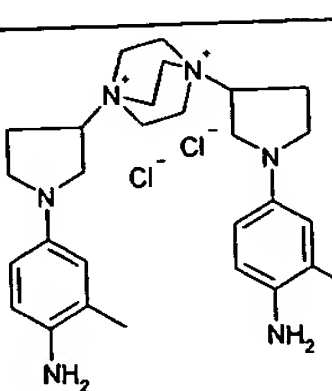
[037] Mention may be made, in formula (I'), of the following examples: n and n' may be 0 or 1, R_1 and R_2 may be chosen from methyl, isopropyl, tert-butyl, hydroxymethyl, 2-hydroxyethyl, 1,2-dihydroxyethyl, methoxy, isopropoxy, 2-hydroxyethoxy and trimethylammoniummethyl radicals and an N-methylimidazoliniummethyl radical, R_6 and R_7 may be chosen from a hydrogen atom, C_1 - C_4 hydroxyalkyl, for example hydroxymethyl, a C_1 - C_4 alkyl radical, for example methyl, a carboxyl radical, a carbamoyl radical, a mono- or di(C_1 - C_4)alkylcarbamoyl radical, for example N,N-dimethylcarbamoyl, a tri(C_1 - C_4)alkylammonium(C_1 - C_4)alkyl radical, for example trimethylammoniummethyl, and an N-alkyl(C_1 - C_4)imidazoliumalkyl radical, R_8 and R_9 may be chosen from a hydrogen atom, a hydroxyl radical, an amino radical, a mono- or di((C_1 - C_4)alkyl)amino radical, for example dimethylamino or bis(2-hydroxyethyl)amino, a C_1 - C_4 alkyl radical, for example methyl, a tri(C_1 - C_4)alkylammonium radical, for example trimethylammonium, and an N-(C_1 - C_4)alkylimidazolinium radical, for example N-methylimidazolinium, A may be chosen from a covalent bond or a radical chosen from:



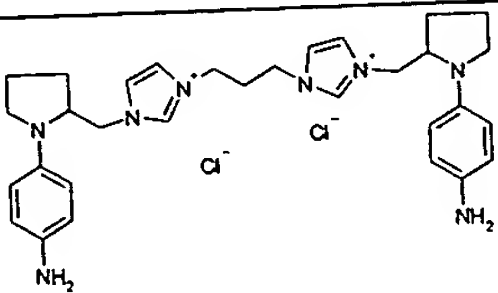
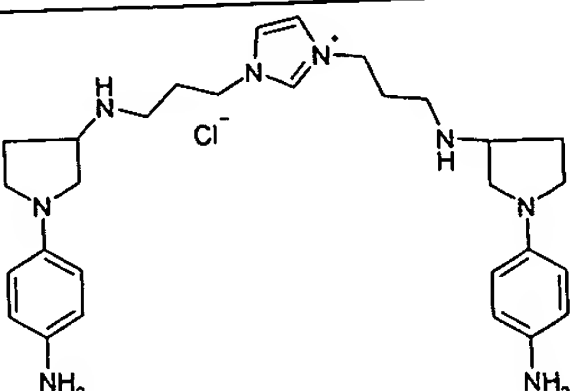
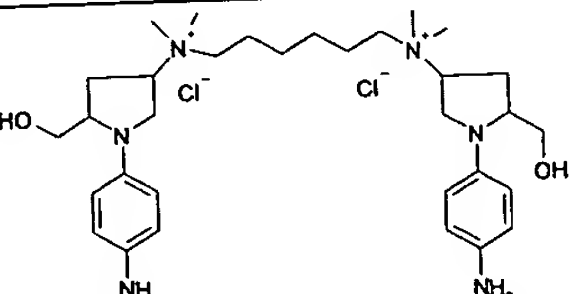
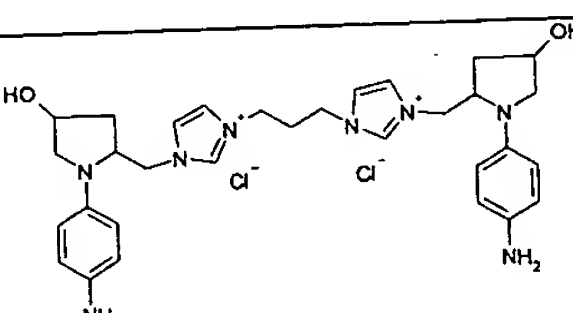
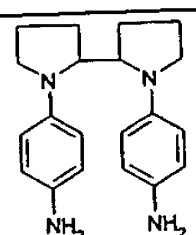
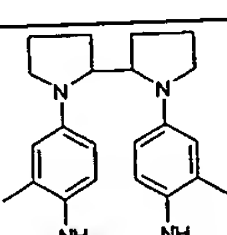
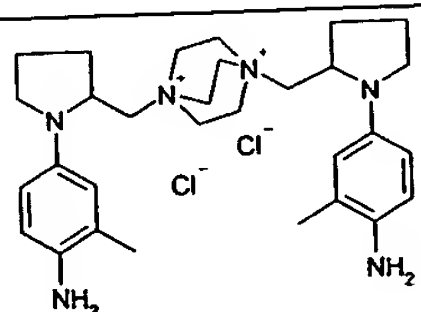
[038] In the context of the present disclosure, the counterion Y may be chosen from halogen atoms, such as bromine, chlorine, fluorine and iodine, hydroxides, citrates, succinates, tartrates, lactates, tosylates, mesylates, benzenesulphonates, acetates, hydrogen sulphates and C₁-C₆ alkyl sulphates, for instance methyl sulphate and/or ethyl sulphate.

[039] Non-limiting examples of derivatives of formula (I) that may be mentioned include:

Structure	Nomenclature
	N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]- N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
	3-[1-(4-aminophenyl)pyrrolidin-3-yl]-1-(6-{1-[1-(4-aminophenyl)pyrrolidin-3-yl]-1H-imidazol-3-ium-3-yl}hexyl)-1H-imidazol-3-ium dichloride
	1,3-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-1H- imidazol-3-ium chloride
	1,4-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-1,4- dimethylpiperazinediium dichloride
	1,4-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-1,4- diazoniabicyclo[2.2.2]octane dichloride
	N,N'-bis{[1-(4-aminophenyl)pyrrolidin-2-yl]methyl}- N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
	3-[[1-(4-aminophenyl)pyrrolidin-2-yl]methyl]-1-[6- (1-[[1-(4-aminophenyl)pyrrolidin-2-yl]methyl]-1H- imidazol-3-ium-3-yl)hexyl]-1H-imidazol-3-ium

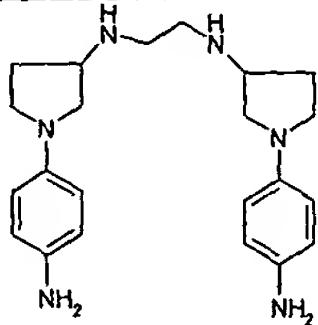
Structure	Nomenclature
	dichloride
	1,4-bis([1-(4-aminophenyl)pyrrolidin-2-yl]methyl)- 1,4-dimethylpiperazinediium dichloride
	N,N'-bis[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]-N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
	3-[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]-1-(6- {1-[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]-1H- imidazol-3-ium-3-yl}hexyl)-1H-imidazol-3-ium dichloride
	1,3-bis[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]- 1H-imidazol-3-ium chloride
	1,4-bis[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]- 1,4-dimethylpiperazinediium dichloride
	1,4-bis[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]- 1,4-diazoniabicyclo[2.2.2]octane dichloride

Structure	Nomenclature
	N,N'-bis[[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl]-N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
	3-[[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl]-1-[6-(1-[[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl])-1H-imidazol-3-ium-3-yl]hexyl]-1H-imidazol-3-ium dichloride
	1,4-bis[[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl]-1,4-dimethylpiperazinediium dichloride
	1,4-bis[[1-(4-aminophenyl)pyrrolidin-2-yl]methyl]-1,4-diazoniabicyclo[2.2.2]octane dichloride
	N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-N,N,N',N'-tetramethylpropane-1,3-diaminium dichloride
	3-[1-(4-aminophenyl)pyrrolidin-3-yl]-1-(3-{1-[1-(4-aminophenyl)pyrrolidin-3-yl]-1H-imidazol-3-ium-3-yl}propyl)-1H-imidazol-3-ium dichloride
	N,N'-bis[[1-(4-aminophenyl)pyrrolidin-2-yl]methyl]-N,N,N',N'-tetramethylpropane-1,3-diaminium dichloride

Structure	Nomenclature
	3-[[1-(4-aminophenyl)pyrrolidin-2-yl]methyl]-1-[3-(1-[[1-(4-aminophenyl)pyrrolidin-2-yl]methyl]-1H-imidazol-3-ium-3-yl)propyl]-1H-imidazol-3-ium dichloride
	1,3-bis(3-[[1-(4-aminophenyl)pyrrolidin-3-yl]amino]propyl)-1H-imidazol-3-ium chloride
	N,N'-bis[1-(4-aminophenyl)-5-(hydroxymethyl)pyrrolidin-3-yl]-N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
	3-[[1-(4-aminophenyl)-4-hydroxypyrrolidin-2-yl]methyl]-1-[3-(1-[[1-(4-aminophenyl)-4-hydroxypyrrolidin-2-yl]methyl]-1H-imidazol-3-ium-3-yl)propyl]-1H-imidazol-3-ium dichloride
	4-[1'-(4-aminophenyl)-2,2'-bipyrrolidin-1-yl]phenylamine
	4-[1'-(4-amino-3-methylphenyl)-2,2'-bipyrrolidin-1-yl]phenylamine
	1,4-bis[[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl]-1,4-diazoniabicyclo[2.2.2]octane dichloride

Structure	Nomenclature
	N,N'-bis[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]-N,N,N',N'-tetramethylpropane-1,3-diaminium dichloride
	3-[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]-1-(3-{1-[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]-1H-imidazol-3-ium-3-yl}propyl)-1H-imidazol-3-ium dichloride
	N,N'-bis{[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl}-N,N,N',N'-tetramethylpropane-1,3-diaminium dichloride
	3-[[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl]-1-[3-(1-{[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl}-1H-imidazol-3-ium-3-yl)propyl]-1H-imidazol-3-ium dichloride
	1,3-bis(3-[[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]amino]propyl)-1H-imidazol-3-ium chloride
	N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-N,N',dipyrrolidinehexane-1,6-diaminium dichloride

Structure	Nomenclature
	N,N'-bis[1-(4-aminophenyl)pyrrolidin-5-amido-3-yl]-N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
	N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]butane-1,2-diamine
	N,N'-bis[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]butane-1,2-diamine
	1,3-bis[[1-(4-aminophenyl)pyrrolidin-2-yl]methoxy]-propane
	1,3-bis[[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methoxy]-propane
	N,N'-bis[[1-(4-aminophenyl)-4-hydroxypyrrolidin-2-yl]methyl]-N,N,N',N'-tetramethylpropane-1,3-diaminium dichloride
	N,N'-bis[1-(4-amino-3-methylphenyl)pyrrolidin-3-yl]ethane-1,2-diamine

Structure	Nomenclature
	<p>N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]ethane-1,2-diamine</p>

[040] For example, non-limiting mention may be made of the compounds of formula (I) chosen from:

- N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
- 3-[1-(4-aminophenyl)pyrrolidin-3-yl]-1-(6-{1-[1-(4-aminophenyl)pyrrolidin-3-yl]-1H-imidazol-3-ium-3-yl}hexyl)-1H-imidazol-3-ium dichloride
- 1,3-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-1H-imidazol-3-ium chloride
- 1,4-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-1,4-dimethylpiperazinediium dichloride
- 1,4-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-1,4-diazoniabicyclo[2.2.2]octane dichloride
- N,N'-bis{[1-(4-aminophenyl)pyrrolidin-2-yl]methyl}-N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
- 3-{[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl}-1-[6-(1-{[1-(4-amino-3-methylphenyl)pyrrolidin-2-yl]methyl}-1H-imidazol-3-ium-3-yl)hexyl]-1H-imidazol-3-ium dichloride
- 1,4-bis{[1-(4-aminophenyl)pyrrolidin-2-yl]methyl}-1,4-dimethylpiperazinediium dichloride
- 1,4-bis{[1-(4-aminophenyl)pyrrolidin-2-yl]methyl}-1,4-diazoniabicyclo[2.2.2]octane dichloride

- N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-N,N,N',N'-tetramethylpropane-1,3-diaminium dichloride
- 3-[1-(4-aminophenyl)pyrrolidin-3-yl]-1-(3-{1-[1-(4-aminophenyl)pyrrolidin-3-yl]-1H-imidazol-3-ium-3-yl}propyl)-1H-imidazol-3-ium dichloride
- N,N'-bis{[1-(4-aminophenyl)pyrrolidin-2-yl]methyl}-N,N,N',N'-tetramethylpropane-1,3-diaminium dichloride
- 3-{[1-(4-aminophenyl)pyrrolidin-2-yl]methyl}-1-[3-(1-{[1-(4-aminophenyl)pyrrolidin-2-yl]methyl}-1H-imidazol-3-ium-3-yl)propyl]-1H-imidazol-3-ium dichloride
- 1,3-bis(3-{[1-(4-aminophenyl)pyrrolidin-3-yl]amino}propyl)-1H-imidazol-3-ium chloride
- N,N'-bis[1-(4-aminophenyl)-5-(hydroxymethyl)pyrrolidin-3-yl]-N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
- 3-{[1-(4-aminophenyl)-4-hydroxypyrrolidin-2-yl]methyl}-1-[3-(1-{[1-(4-aminophenyl)-4-hydroxypyrrolidin-2-yl]methyl}-1H-imidazol-3-ium-3-yl)propyl]-1H-imidazol-3-ium dichloride
- 4-[1'-(4-aminophenyl)-2,2'-bipyrrolidin-1-yl]phenylamine
- N,N'-bis[1-(4-aminophenyl)pyrrolidin-5-amido-3-yl]-N,N,N',N'-tetramethylhexane-1,6-diaminium dichloride
- N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]butane-1,2-diamine
- 1,3-bis{[1-(4-aminophenyl)pyrrolidin-2-yl]methoxy}propane
- N,N'-bis{[1-(4-aminophenyl)-4-hydroxypyrrolidin-2-yl]methyl}-N,N,N',N'-tetramethylpropane-1,3-diaminium dichloride
- N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]ethane-1,2-diamine

- N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-N,N'-dipyrrolidinehexane-1,6-diaminium dichloride.

[041] The dye composition of the present disclosure comprises, in a cosmetic medium that is suitable for dyeing keratin fibres, such as human hair, as the at least one oxidation base, a derivative of formula (I) as defined above.

[042] The oxidation base(s) of the disclosure is (are) each generally present in an amount ranging approximately from 0.001% to 10%, by weight, relative to the total weight of the dye composition, and for example from 0.005% to 6%.

[043] The dye composition of the disclosure may contain one or more couplers conventionally used for dyeing keratin fibres. Among these couplers, mention may be made of meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalenic couplers and heterocyclic couplers, and the addition salts thereof.

[044] Further examples that may be mentioned include 2-methyl-5-aminophenol, 5-N-(β -hydroxyethyl)amino-2-methylphenol, 6-chloro-2-methyl-5-aminophenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β -hydroxyethyloxy)benzene, 2-amino-4-(β -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-dimethylaminobenzene, sesamol, 1- β -hydroxyethylamino-3,4-methylenedioxybenzene, α -naphthol, 2-methyl-1-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 1-N-(β -hydroxyethyl)amino-3,4-methylenedioxybenzene and 2,6-bis(β -hydroxyethylamino)toluene and the addition salts thereof with an acid.

[045] In the composition of the present disclosure, the coupler(s) is(are) generally present in an amount ranging approximately from 0.001% to 10% by weight, relative to the total weight of the dye composition, for instance, from 0.005% to 6%.

[046] The composition of the present disclosure may also comprise at least one additional oxidation base conventionally used in oxidation dyeing, other than those described above. By way of example, these additional oxidation bases may be chosen from para-phenylenediamines other than those described above, bis(phenyl)alkylenediamines, para-aminophenols, bis-para-aminophenols, ortho-aminophenols, heterocyclic bases, and the addition salts thereof.

[047] Among the para-phenylenediamines which may be mentioned, for example, are para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(β -hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β -hydroxyethyl)amino-2-chloroaniline, 2- β -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-(β -hydroxyethyl)-para-phenylenediamine, N-(β,γ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2- β -acetylaminioethyloxy-para-phenylenediamine, N-(β -methoxyethyl)-para-phenylenediamine, 4-aminophenylpyrrolidine, 2-thienyl-para-phenylenediamine, 2- β -hydroxyethylamino-

5-aminotoluene and 3-hydroxy-1-(4'-aminophenyl)pyrrolidine, and the addition salts thereof with an acid.

[048] Among the para-phenylenediamines, further mention may be made of para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2- β -hydroxyethyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2- β -acetylaminoethyloxy-para-phenylenediamine, and the addition salts thereof with an acid.

[049] Among the bis(phenyl)alkylenediamines which can be mentioned, for example, are N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4'-aminophenyl)tetramethylenediamine, N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)tetramethylenediamine, N,N'-bis(4-methyl-aminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane, and the addition salts thereof with an acid.

[050] Among the para-aminophenols which can be mentioned, for example, are para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

[051] Among the ortho-aminophenols which can be mentioned, for example, are 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

[052] Among the heterocyclic bases, mention may be made, for example, of pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

[053] Among the pyridine derivatives which may be mentioned are the compounds described, for example, in patents GB 1 026 978 and GB 1 153 196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β -methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid.

[054] Other pyridine oxidation bases that are useful according to the present disclosure are the 3-aminopyrazolo[1,5-a]pyridine oxidation bases or the addition salts thereof described, for example, in patent application FR 2 801 308. By way of example, mention may be made of pyrazolo[1,5-a]pyrid-3-ylamine; 2-acetylaminopyrazolo[1,5-a]pyrid-3-ylamine; 2-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine; 3-aminopyrazolo[1,5-a]pyridine-2-carboxylic acid, 2-methoxypyrazolo[1,5-a]pyrid-3-ylamine; (3-aminopyrazolo[1,5-a]pyrid-7-yl)methanol; 2-(3-aminopyrazolo[1,5-a]pyrid-5-yl)ethanol; 2,3-aminopyrazolo[1,5-a]pyrid-7-yl)ethanol; (3-aminopyrazolo[1,5-a]pyrid-2-yl)-methanol; 3,6-diaminopyrazolo[1,5-a]pyridine; 3,4-diaminopyrazolo[1,5-a]pyridine; pyrazolo[1,5-a]pyridine-3,7-diamine; 7-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine; pyrazolo[1,5-a]pyridine-3,5-diamine; 5-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine; 2-[(3-aminopyrazolo[1,5-a]pyrid-5-yl)(2-hydroxyethyl)amino]ethanol; 2-[(3-aminopyrazolo[1,5-a]pyrid-7-yl)(2-hydroxyethyl)amino]ethanol; 3-aminopyrazolo[1,5-a]pyrid-5-ol; 3-aminopyrazolo[1,5-a]pyrid-4-ol; 3-aminopyrazolo[1,5-a]pyrid-6-ol;

3-aminopyrazolo[1,5-a]pyrid-7-ol and also the addition salts thereof with an acid or with a base.

[055] Among the pyrimidine derivatives which may be mentioned are the compounds described, for example, in patent DE 2 359 399 or patents JP 88-169 571; JP 05 63 124; EP 0 770 375 or patent application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine, and pyrazolopyrimidine derivatives such as those mentioned in patent application FR-A-2 750 048 and among which mention may be made of pyrazolo[1,5-a]pyrimidine-3,7-diamine; 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine; pyrazolo[1,5-a]pyrimidine-3,5-diamine; 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine; 3-aminopyrazolo[1,5-a]pyrimidin-7-ol; 3-aminopyrazolo[1,5-a]pyrimidin-5-ol; 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxyethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 3-amino-5-methyl-7-imidazolylpropylamino-pyrazolo[1,5-a]pyrimidine, and the addition salts thereof with an acid and the tautomeric forms thereof, when a tautomeric equilibrium exists.

[056] Among the pyrazole derivatives which may be mentioned are the compounds described in patents DE 3 843 892 and DE 4 133 957 and patent applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-(β -hydroxyethyl)pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-

phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4-(β -hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof with an acid.

[057] The oxidation base(s) present in the composition of the invention is (are) each generally present in an amount ranging approximately from 0.001% to 10% by weight, relative to the total weight of the dye composition, for example from 0.005% to 6%.

[058] In general, the addition salts of the oxidation bases and of the couplers that may be used in the context of the invention are chosen, for instance, from the addition salts with an acid, such as the hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates, tosylates, benzenesulphonates, phosphates and acetates, and the addition salts with a base, such as sodium hydroxide, potassium hydroxide, ammonia, amines or alkanolamines.

[059] The dye composition in accordance with the disclosure may also contain one or more direct dyes that may be chosen from, for example, nitrobenzene dyes, azo direct dyes and non-ionic direct dyes. These direct dyes may be of non-ionic, anionic or cationic nature.

[060] The medium that is suitable for dyeing, also known as the dye support, generally comprises water or a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently soluble in water. As organic solvents, mention may be made, for example, of C₁-C₄ lower alkanols, such as ethanol and isopropanol; polyols and polyol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, as well as aromatic alcohols such as benzyl alcohol or phenoxyethanol, and mixtures thereof.

[061] For example, the solvents may be present in an amount ranging approximately from 1% to 40% by weight, relative to the total weight of the dye composition, for instance from 5% to 30% by weight.

[062] The dye composition in accordance with the disclosure can also contain various adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, non-ionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, non-ionic, amphoteric or zwitterionic polymers or mixtures thereof, inorganic or organic thickeners, and, for example, anionic, cationic, non-ionic or amphoteric associative polymeric thickeners, antioxidants, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, packaging agents such as, for example, silicones, which may or may not be volatile or modified, film-forming agents, ceramides, preserving agents and opacifiers.

[063] The above adjuvants are generally present in an amount for each adjuvant ranging from 0.01% to 20% by weight, relative to the weight of the composition.

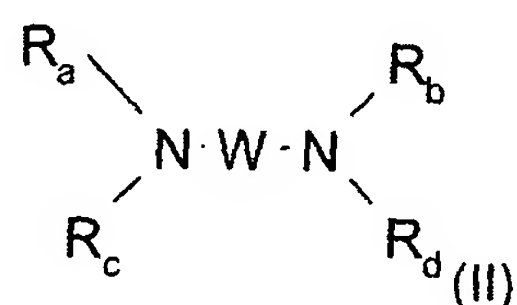
[064] Needless to say, a person skilled in the art will take care to select this or these optional additional compounds such that the beneficial properties intrinsically

associated with the oxidation dye composition in accordance with the disclosure are not, or are not substantially, adversely affected by the addition(s) envisaged.

[065] The pH of the dye composition in accordance with the invention generally ranges from about 3 to 12, and for example, from about 5 to 11. It may be adjusted to the desired value using acidifying or basifying agents usually used in the dyeing of keratin fibres, or alternatively using standard buffer systems.

[066] Among the acidifying agents which may be mentioned, for example, are inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid and lactic acid, and sulphonic acids.

[067] Among the basifying agents which may be mentioned, for example, are aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (II) below:



wherein: W is a propylene residue which is unsubstituted or substituted with a hydroxyl group or a C₁-C₄ alkyl radical; R_a, R_b, R_c and R_d, which may be identical or different, are chosen from hydrogen atoms, C₁-C₄ alkyl radicals and C₁-C₄ hydroxyalkyl radicals.

[068] The dye composition according to the present disclosure may be in various forms, such as in the form of liquids, creams or gels, or in any other form that is suitable for dyeing keratin fibres, for example human hair.

[069] The process disclosed herein is a process wherein the composition according to the present disclosure as described above is applied to the fibres, in the presence of an oxidizing agent for a time that is sufficient to develop the desired colour. The colour may be developed at acidic, neutral or alkaline pH and the oxidizing agent may be added to the composition of the disclosure just at the time of use, or it may be used starting with an oxidizing composition containing it, which is applied simultaneously or sequentially to the composition of the disclosure.

[070] According to one aspect of the disclosure, the composition is mixed, for instance, at the time of use, with a composition comprising, in a medium that is suitable for dyeing, at least one oxidizing agent, this oxidizing agent being present in an amount that is sufficient to develop a coloration. The mixture obtained is then applied to the keratin fibres. After an action time ranging from 3 to 50 minutes approximately, for example, 5 to 30 minutes approximately, the keratin fibres are rinsed, washed with shampoo, rinsed again and then dried.

[071] The oxidizing agents conventionally used for the oxidation dyeing of keratin fibres are, for example, hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulphates, peracids and oxidase enzymes, among which mention may be made of peroxidases, 2-electron oxidoreductases such as uricases, and 4-electron oxygenases, for instance laccases. For example, mention may be made of hydrogen peroxide. The oxidizing agent may also be atmospheric oxygen.

[072] The oxidizing composition may also comprise various adjuvants conventionally used in compositions for dyeing the hair and as defined above.

[073] The pH of the oxidizing composition comprising the oxidizing agent is such that, after mixing with the dye composition, the pH of the resulting composition applied to

the keratin fibres ranges for example, from 3 to 12 approximately such as, from 5 to 11. It may be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres and as defined above.

[074] The ready-to-use composition that is finally applied to the keratin fibres may be in various forms, such as in the form of liquids, creams or gels or any other form that is suitable for dyeing keratin fibres, for instance human hair.

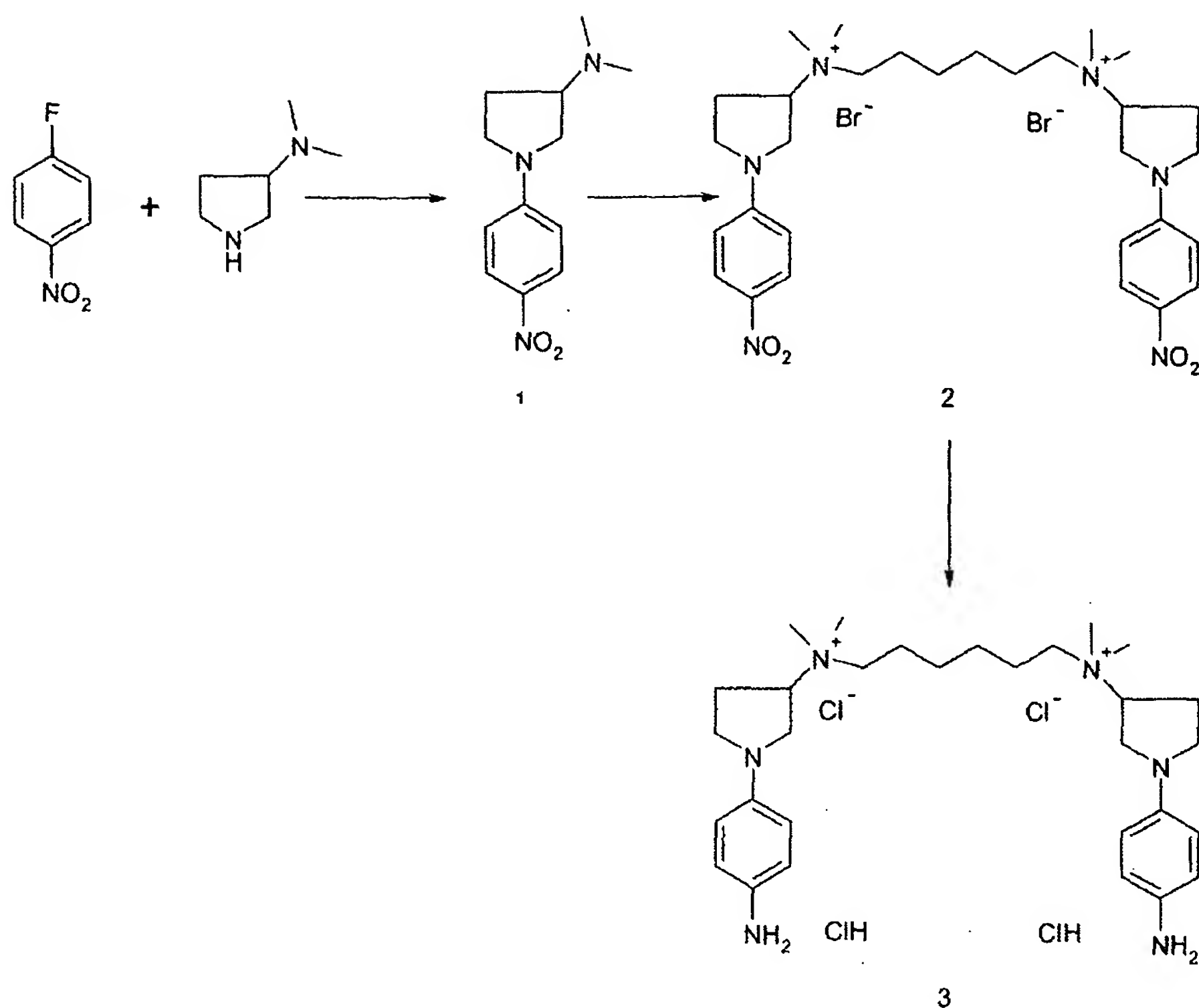
[075] Another aspect of the disclosure is a multi-compartment dyeing device or "kit", in which at least one compartment contains the dye composition as disclosed herein, and at least one other compartment contains an oxidizing composition. This device may be equipped with a means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

[076] Using this device, it is possible to dye keratin fibres using a process that includes mixing a dye composition comprising at least one oxidation base of formula (I) with an oxidizing agent, and applying the mixture obtained to the keratin fibres for a time that is sufficient to develop the desired coloration.

[077] The examples that follow serve to illustrate the disclosure without, however, being limiting in nature.

EXAMPLES

Example 1: Synthesis of N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-N,N'-trimethylhexane-1,6-diammonium chloride hydrochloride (3)



Synthesis of N,N'-bis[1-(4-nitrophenyl)pyrrolidin-3-yl]-N,N'-trimethylhexane-1,6-diammonium bromide (2)

[078] 0.513 g (0.00218 mol) of [1-(4-nitrophenyl)pyrrolidin-3-yl]dimethylamine and 0.244 g (0.001 mol) of dibromohexane were refluxed in 10 ml of methanol for six hours. After cooling to room temperature, the precipitate was washed with ethyl acetate and then filtered off. After draining by suction and drying the precipitate, 1.5 g of yellow powder (2) were obtained.

^1H NMR (400 MHz-DMSO) ppm 8.12 (d, 4H); 6.75 (d, 4H); 5.48 (m, 2H); 3.94 (m, 2H); 3.75 (m, 4H); 3.44 (m, 7H); 3.13 (s, 12H); 2.51-2.44 (m, 4H); 1.81 (m, 4H); 1.39 (m, 4H).

Mass ESI+: $m/z=277$ [$M_2+1/2$]

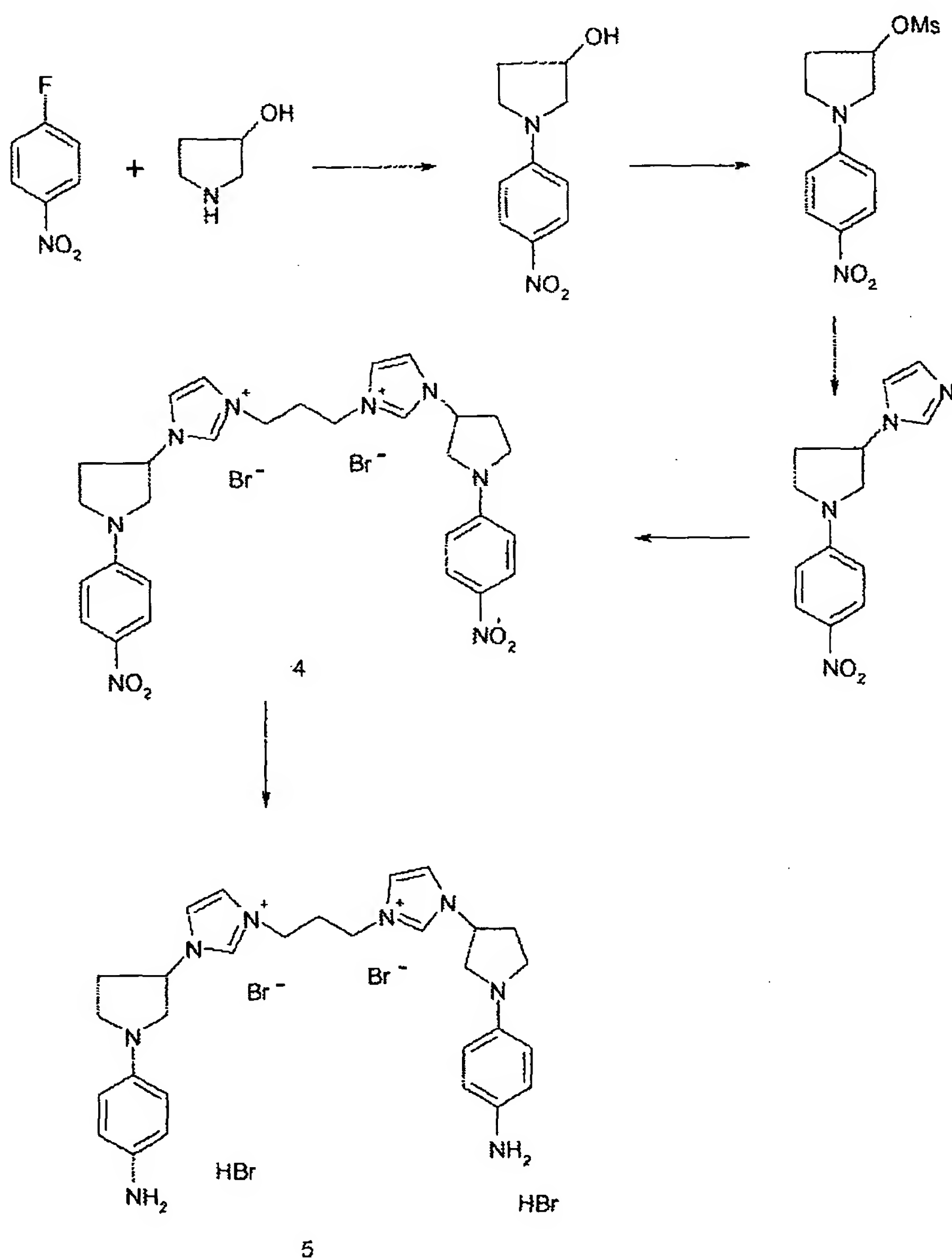
Synthesis of N,N'-bis[1-(4-aminophenyl)pyrrolidin-3-yl]-N,N'-trimethylhexane-1,6-diammonium chloride (3)

[079] 1.5 g (0.0021 mol) of derivative (2) above dissolved in 250 ml of ethanol/water (50/50) were hydrogenated in the presence of palladium-on-charcoal under a hydrogen pressure of 10 bar, while heating to 65°C; after filtering of the catalyst, the expected derivative (3) was isolated in the form of the hydrochloride. 1 g of white powder is obtained.

¹H NMR (400 MHz-D₂O) ppm: 7.20 (d, 2H); 6.72 (d, 2H); 4.31 (m, 2H); 3.70 (m, 2H); 3.55 (m, 4H); 3.33 (m, 4H); 3.21 (m, 2H); 3.03 (bs, 12H); 2.40 (m, 4H); 1.79 (m, 4H); 1.37 (m, 4H).

Mass ESI+: m/z=247 [M₂+/2]

Example 2: Synthesis of 3-[1-(4-aminophenyl)pyrrolidin-3-yl]-1-(3-{1-[1-(4-aminophenyl)pyrrolidin-3-yl]-1H-imidazol-3-ium-3-yl}propyl)-1H-imidazol-3-ium dibromide



Synthesis of 3-[1-(4-nitrophenyl)pyrrolidin-3-yl]-1-(3-{1-[1-(4-nitrophenyl)pyrrolidin-3-yl]-1H-imidazol-3-ium-3-yl}propyl)-1H-imidazol-3-ium dibromide (4)

[080] 3.5 g (0.0135 mol) of 1-[1-(4-nitrophenyl)pyrrolidin-3-yl]-1H-imidazole were heated to 100°C in 12 ml of a pentanol/DMF mixture (50/50). 1 g (0.005 mol) of dibromopropane was added. The reaction medium was heated at 115°C for 17 hours. The precipitate was filtered off while hot and washed with pentanol and then with ether. After draining by suction and drying the precipitate, 3.4 g of yellow powder (4) were obtained. 33% yield.

¹H NMR (400 MHz-DMSO) ppm: 9.41 (s, 2H); 8.13 (d, J=9 Hz, 4H); 7.93 (m, 2H); 7.88 (m, 2H); 6.71 (d, J=9 Hz, 4H); 5.30 (m, 2H); 4.25 (m, 4H); 3.98 (m, 2H); 3.83 (m, 2H); 3.70 (m, 2H); 3.60 (m, 2H); 2.46-2.40 (m, 6H).

Mass ESI+: m/z=639 [M²⁺ + Br⁻]⁺, 557 [M²⁺ = Br⁻ - HBr]⁺

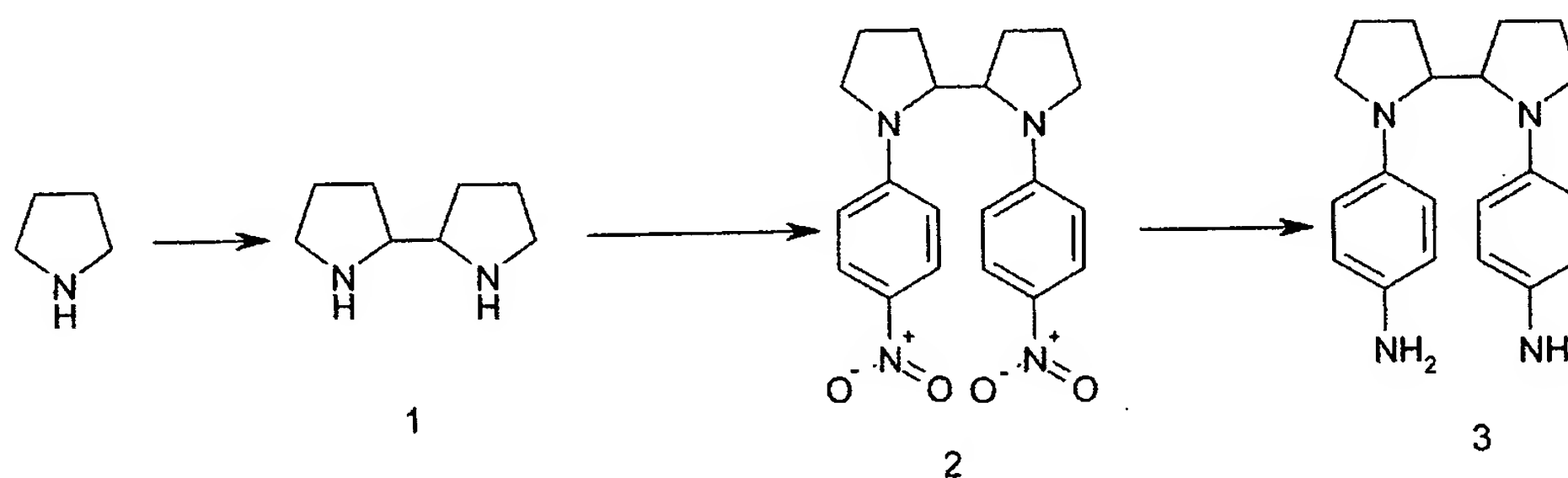
Synthesis of 3-[1-(4-aminophenyl)pyrrolidin-3-yl]-1-(3-{1-[1-(4-aminophenyl)pyrrolidin-3-yl]-1H-imidazol-3-ium-3-yl}propyl)-1H-imidazol-3-ium dibromide (5)

[081] 3.2 g (0.0044 mol) of derivative (4) above dissolved in a mixture of 60 ml of water/300 ml of ethanol were hydrogenated in the presence of palladium-on-charcoal under a hydrogen pressure of 9 bar and at 75°C. After filtering off the catalyst, the expected derivative (5) was isolated in the form of the hydrobromide. 3.4 g of white powder were obtained; 94% yield.

^1H NMR (400 MHz-DMSO) ppm: 8.84 (s, 2H); 7.41 (s, 2H); 7.41 (s, 2H); 7.17 (d, 4H); 6.69 (d, 4H); 5.14 (m, 2H); 4.22 (t, 4H); 3.69 (dd, 2H); 3.62 (dd, 2H); 3.55 (m, 2H); 3.34 (m, 2H); 2.59 (m, 2H); 2.42 (m, 2H); 2.3 (m, 2H).

Mass ESI+: $m/z=579$ $[\text{M}^{2+} + \text{Br}^-]^+$, 249 $[\text{M}]^{2+}/2$

Example 3: Synthesis of 1,1'-bis(4-aminophenyl)[2,2']bipyrrolidiny-1-yl



Preparation of [2,2']bipyrrolidiny-1-yl (1)

[082] 108 g (1.52 mol) of pyrrolidine and 11 g (0.076 mol) of di-*t*-butyl peroxide were heated in a stainless-steel autoclave at 140°C for 9 hours. The reaction medium was evaporated to dryness and then treated with sodium borohydride in ethanol for 1 hour. After evaporating off the ethanol, the product was extracted with ethyl acetate and washed with water. On concentration, 2.6 g (80%) of a brown oil were obtained, which product was used without further modification for the rest of the synthesis.

Preparation of 1,1'-bis(4-nitrophenyl)[2,2']bipyrrolidiny-1-yl (2)

[083] 2.6 g (~15 mmol) of [2,2']bipyrrolidiny-1-yl (1) obtained above were refluxed in the presence of 5 g (35.7 mmol) of potassium carbonate and 5 g (35.7 mmol) of para-

fluoronitrobenzene in 25 ml of water overnight. The agglomerate formed was filtered off and then rinsed with acetone and isopropanol to give 2.15 g of a mixture of two isomers (55/45) (44%). After purification by chromatography on silica gel, a majority isomer was isolated (1.2 g), the analyses for which were:

¹H NMR (400 MHz, DMSO): 1.92 (m, 2H, CH₂ 3'); 1.98 (m, 2H, CH₂ 4'); 2.11 (m, 2H, CH₂ 4'); 2.48 (m, 2H, CH₂ 3'); 3.14 (m, 2H, 1H, CH₂ 2'); 3.55 (m, 2H, CH₂ 2'); 4.13 (m, 2H, CH 5'); 6.39 (d, 4H, H₂-H₆); 7.81 (d, 4H, H₃-H₅).

Mass ESI+: m/z = 383 (M+H)⁺

Preparation of 1,1'-bis(4-aminophenyl)[2,2']bipyrrolidinyl (3)

[084] The derivative (2) was dissolved in 300 ml of ethanol and then hydrogenated in the presence of zinc. The expected derivative (3) was isolated in the form of the hydrochloride after acidifying the filtrate with hydrochloric acid.

EXAMPLES 1 TO 4 OF DYEING IN ALKALINE MEDIUM

Examples	1	2	3	4
N,N'-Bis[1-(4-aminophenyl)-pyrrolidin-3-yl]-N,N'-trimethylhexane-1,6-diammonium chloride hydrochloride (base)	10 ⁻³ mol	10 ⁻³ mol	10 ⁻³ mol	10 ⁻³ mol
2-(2,4-Diaminophenoxy)ethanol dihydrochloride (coupler)	10 ⁻³ mol	-	-	-
3-Amino-2-chloro-6-	-	10 ⁻³ mol	-	-

methylphenol hydrochloride (coupler)				
3,6-Dimethyl-1H- pyrazolo[5,1-c][1,2,4]triazole (coupler)	-	-	10^{-3} mol	-
2-Methyl-5-aminophenol (coupler)	-	-	-	10^{-3} mol
Dye support (1)	(*)	(*)	(*)	(*)
Demineralized water qs	100 g	100 g	100 g	100 g

(*) Dye support (1) pH 9.5

96° ethyl alcohol	20.8 g
Sodium metabisulphite as an aqueous 35% solution	0.23 g A.M.
Pentasodium salt of diethylenetriaminepentaacetic acid as an aqueous 40% solution	0.48 g A.M.
C ₈ -C ₁₀ alkyl polyglucoside as an aqueous 60% solution	3.6 g A.M.
Benzyl alcohol	2.0 g
Polyethylene glycol containing 8 units of ethylene oxide	3.0 g

NH ₄ Cl	4.32 g
Aqueous ammonia containing 20% NH ₃	2.94

[085] At the time of use, each composition was mixed with an equal weight of 20-volumes aqueous hydrogen peroxide solution (6% by weight). A final pH of 9.5 was obtained.

[086] Each mixture obtained was applied to locks of grey hair containing 90% white hairs. After leaving to act for 30 minutes, the locks were rinsed, washed with a standard shampoo, rinsed again and then dried.

[087] The following dyeing results were obtained.

Examples	1	2	3	4
Shade observed	violet-blue	blue-violet	red-violet	violet

EXAMPLES 5 TO 7 OF DYEING IN ACIDIC MEDIUM

[088] The dye compositions below were prepared:

Example	5	6	7
N,N'-Bis[1-(4-aminophenyl)pyrrolidin-3-yl]-N,N'-trimethylhexane-1,6-diammonium chloride hydrochloride (base)	10 ⁻³ mol	10 ⁻³ mol	10 ⁻³ mol

2-(2,4-Diaminophenoxy)ethanol dihydrochloride (coupler)	10^{-3} mol	-	-
3-Amino-2-chloro-6-methylphenol hydrochloride (coupler)	-	10^{-3} mol	
2-Methyl-5-aminophenol (coupler)	-	-	10^{-3} mol
Dye support (2)	(*)	(*)	(*)
Demineralized water qs	100 g	100 g	100 g

(*) Dye support (2) pH 7

96° ethyl alcohol	20.8 g
Sodium metabisulphite as an aqueous 35% solution	0.23 g A.M.
Pentasodium salt of diethylenetriaminepentaacetic acid as an aqueous 40% solution	0.48 g A.M.
C ₈ -C ₁₀ alkyl polyglucoside as an aqueous 60% solution	3.6 g A.M.
Benzyl alcohol	2.0 g
Polyethylene glycol containing 8 units of ethylene oxide	3.0 g
Na ₂ HPO ₄	0.28 g
KH ₂ PO ₄	0.46 g

[089] At the time of use, each composition was mixed with an equal weight of 20-volumes aqueous hydrogen peroxide solution (6% by weight). A final pH of 7 was obtained.

[090] Each mixture obtained was applied to locks of grey hair containing 90% white hairs. After leaving to act for 30 minutes, the locks were rinsed, washed with a standard shampoo, rinsed again and then dried.

[091] The following dyeing results were obtained.

Examples	5	6	7
Shade observed	violet-blue	blue-violet	violet